

410 Rec'd PCT/PTO 26 SEP 2000

FORM PTO-1390
(REV 10-94)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

DOCKET #: 3395-4PUS

**TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING
UNDER 35 U.S.C. 371**

**U.S. APPLICATION NO.
(If known, see 37 CFR 1.5)**
09/647108

INTERNATIONAL APPLICATION NO.
PCT/EP99/02008

INTERNATIONAL FILING DATE
24 March 1999

PRIORITY DATE CLAIMED
26 March 1998

TITLE OF INVENTION

Method for Reducing The Availability Of Heavy Metal Nutrients And The Use Of Cross Linked Poly(Meth)Acrylates In Said Method

APPLICANT(S) FOR DO/EO/US

Aloys HÜTTERMANN; Moitoba ZOMORRODI

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371
3. This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. has been transmitted by the International Bureau.
 - c. is not required, as the application was filed in the United States Receiving Office (RO/US)
6. A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. have been transmitted by the International Bureau.
 - c. have not been made; however, the time limit for making such amendments has NOT expired.
 - d. have not been made and will not be made.
8. A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. Below concern other document(s) or information included:

11. An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. A **FIRST** preliminary amendment.
14. A **SECOND** or **SUBSEQUENT** preliminary amendment.
15. A substitute specification.
16. A change of power of attorney and/or address letter.
16. Other items or information (*specify*): PCT Publication Sheet, Int'l Preliminary Examination Report, Written Opinion, Int'l Search Report, PCT Request, Letter with Proposed Drawing Changes

17. [x] The following fees are submitted:

Basic National Fee (37 CFR 1.492(a)(1)-(5)):

Search Report has been prepared by the EPO or JPO \$840.00
 International preliminary examination fee paid to USPTO (37 CFR 1.482).....\$670.00
 No international preliminary examination fee paid to USPTO (37 CFR 1.482)
 but international search fee paid to USPTO (37 CFR 1.445(a)(2)) \$760.00
 Neither international preliminary examination fee (37 CFR 1.482)
 nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$970.00
 International preliminary examination fee paid to USPTO (37 CFR 1.482)
 and all claims satisfied provisions of PCT Article 33(2)-(4).....\$96.00

ENTER APPROPRIATE BASIC FEE AMOUNT =

\$ 840.00

Surcharge of **\$130.00** for furnishing the oath or declaration later than [] 20 [] 30 months from the earliest claimed priority date (37 CFR 1.492(e)).

\$

Claims	Number Filed	Number Extra	Rate	
Total Claims	18 - 20 =	0	x \$18.00	\$
Independent Claims	1 - 3 =	0	x \$78.00	\$
Multiple dependent claim(s) (if applicable)			+ \$260.00	\$
TOTAL OF ABOVE CALCULATIONS =				\$ 840.00
Reduction of $\frac{1}{2}$ for filing by small entity, if applicable. Verified Small Entity statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28).				\$
SUBTOTAL =				\$ 840.00
Processing fee of \$130.00 for furnishing the English translation later than [] 20 [] 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$ +
TOTAL NATIONAL FEE =				\$
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by the appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property				\$ +
TOTAL FEES ENCLOSED				\$ 840.00
				Amount to be refunded: \$
				charged: \$

- a. [x] One check in the amount of \$ 840 to cover the above fees is/are enclosed.
- b. [] Please charge my Deposit Account No. 03-2412 in the amount of \$ _____ to cover the above fees. A duplicate copy of this sheet is enclosed.
- c. [x] The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 03-2412. A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

Thomas C. Pontani

Cohen, Pontani, Lieberman & Pavane
551 Fifth Avenue, Suite 1210
New York, New York 10176

Thomas C. Pontani

Registration Number: 29,763

Tel: (212) 687-2770

09/647108
529 Rec'd PCT/PTC 26 SEP 2000

By Express Mail # EL489905638US · September 26, 2000

Attorney Docket # 3395-4PUS

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re National Phase PCT Application of

Aloys HÜTTERMANN et al.

International Appln. No.: PCT/EP99/02008

International Filing Date: 24 March 1999

For: Method for Reducing The Availability Of Heavy
Metal Nutrients And The Use Of Cross Linked
Poly(Meth)Acrylates In Said Method

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents

Washington, D.C. 20231

BOX PCT

SIR:

Prior to examination of the above-identified application please amend the application as follows:

In the Specification:

Page 1, before the first line insert the Title -- Method Of Reducing The Availability Of Heavy Metals In Plants And The Use Of Cross Linked Poly(Meth)Acrylates In Said Method --;

Lines 2 and 3, delete "and the use of cross linked poly(meth)acrylates in said process";

After line 2 please insert the following subtitle: -- Field of the Invention --;

After line 5, please insert the following subtitle: -- Background of the Invention --;

Line 13, delete "metre" and insert -- meter --;

After line 28 please insert the following subtitle: -- Summary of the Invention --.

Page 2, after line 3, please insert the following subtitle: -- Brief Description of the Presently Preferred Embodiments --.

Page 4, line 5, change "0,01" to -- 0.01 --.

Page 6, line 14 after "treated with" delete "Stockabsorb" and insert instead -- Stockabsorb® (Stockabsorb® is a trademark of and a commercially available acrylamide/acrylic acid copolymer of the instant assignee Stockhausen GmbH & Co. KG, 25 Bäkerpfad, 47805 Krefeld, Germany) --

Page 7, after line 7, please insert the following subtitle: -- Brief Description of the Drawings --;

After line 11 add the following new paragraphs: -- Fig. 5 shows the lead content in the cell wall; and

Fig. 6 shows the root stock of spruce grown in lead-contaminated soil treated and untreated. --.

In the Claims:

Delete claims 1 and 12, amend claims 2-11 as follows:

2. (Amended) The process [Process] according to [Claim 1, characterized in that the substrates are] Claim 12, wherein the soil is treated by [means of] mixing the compound into the soil.

3. (Amended) The process [Process] according to Claim 2, [characterized in that in mixing,] wherein the compound is added in the amount of [additive is] 0.1 to 2.5% by weight.

4. (Amended) The process [Process] according to Claim 3, [characterized in that in mixing,] wherein the compound is added in the amount of [additive is] 0.5 to 2.0% by weight.

5. (Amended) The process [Process] according to [Claim 1, characterized in that] Claim 12, wherein the cross-linked poly(meth)acrylates are produced by using monoethylenically unsaturated monocarboxylic acids[, in particular acrylic acid or its salts].

6. (Amended) The process [Process] according to Claim [5] 12, [characterized in that] wherein the poly(meth)acrylates are produced by using [other] monoethylenically unsaturated monomers containing no carboxylate groups[, in particular by using acrylamide].

7. (Amended) The process [Process] according to [Claims 5 or 6, characterized in that] Claim 5, wherein the poly(meth)acrylates are obtained by using methylenbis(meth)acrylamide, ethylenbis(meth)acrylamide, N-methylolacrylamide or triallylamin as cross-linking agents[, whereby methylenbisacrylamide is preferred].

8. (Amended) The process [Process] according to [one or more of Claims 5 to 7, characterized in that] Claim 5, wherein the poly(meth)acrylates are treated with a subsequent cross-linking agent in quantities of 0.01 to 10% by weight, at an increased temperature[, preferably between 80 and 250°C].

9. (Amended) The process [Process] according to [one or more of Claims 5 to 8, characterized in that] Claim 5, wherein the acidic monomer components of the poly(meth)acrylate are neutralized between 10 and 95 mol percent[, preferably between 50 and 90 mol percent].

10. (Amended) The process [Process] according to [one or more of Claims 5 to 9, characterized in that] Claim 5, wherein the poly(meth)acrylates have an absorption capacity for synthetic soil solution of more than 30 g/g[, preferably more than 50 g/g, and especially more than 65 g/g].

11. (Amended) The process [Process] according to [one or more of Claims 5 to 10, characterized in that] Claim 5, wherein the poly(meth)acrylates are worked into the acid soil up to a depth of about 50 cm.

Please add the following new claims:

-- 12. (New) A process for reducing the presence of heavy metals in plants growing in soil contaminated with heavy metals, comprising: applying to the contaminated soil a heavy metal reducing effective amount of a compound selected from the group consisting of cross-linked polyacrylates and polymethylacrylates.

13. (New) The process according to claim 5, wherein the monocarboxylic acid is acrylic acid or its salts.

14. (New) The process according to claim 6, wherein the monoethylenically unsaturated monomer is acrylamide.

15. (New) The process according to claim 7, wherein the poly(meth)acrylates are obtained by using methylenebisacrylamide.

16. (New) The process according to claim 8, wherein the temperature is between 80°C and 250°C.

17. (New) The process according to claim 9, wherein the acidic monomer components are neutralized between 50 and 90 mol percent.

18. (New) The process according to claim 10, wherein the absorption capacity is more than 50 g/g.

19. (New) The process according to claim 10, wherein the absorption capacity is more than 65 g/g. --

In the Abstract:

Page 10, line 3, change "Abstract" to -- Abstract of the Disclosure --;

Line 5, change "is characterized in that" to , wherein --.

REMARKS

This preliminary amendment is presented to place the application in proper form for examination and to eliminate multiple dependency from the present claims. No new matter has been added. Early examination and favorable consideration of the above-identified application is earnestly solicited.

Any additional fees or charges required at this time in connection with the application may be charged to our Patent and Trademark Office Deposit Account No. 03-2412.

Respectfully submitted,
COHEN, PONTANI, LIEBERMAN & PAVANE

By:


Thomas C. Pontani
Reg. No. 29,763
551 Fifth Avenue, Suite 1210
New York, N.Y. 10176
(212) 687-2770

26 September 2000

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Process for reducing the plant availability of heavy metals and the use of cross-linked poly(meth)acrylates in said process

The invention relates to a process for reducing plant availability of heavy metals and the use of cross-linked poly(meth)acrylates in said process.

Until now, no method is known by which it has been possible to eliminate the effect of heavy metals on plants in soils contaminated with heavy metals.

At present, two methods are used for planting crops in fields containing heavy metals: either top soil is added to the contaminated soils, or the contaminated soil is stripped away and replaced by top soil, in which case the new top soil layer must usually be more than one metre in thickness. Both these methods require much effort and are very expensive.

Experiments conducted so far to reduce plant availability of heavy metals by adding polyacrylates have either been unsuccessful (O.A. El-Hady, A.A. Lotfy, B.M.A. El-Hady, Egyptian Journal of Soil Science, 30:4, 545-557, 1990) or had the effect that the availability of heavy metals such as lead, nickel, manganese or iron was clearly increased (R.L. Mikkelsen, Fertiliser Research 41, 87-92 [1995]; J.J. Mortvedt, R.L. Mikkelsen, J.H. Kelsoc, Soil Science Society of America Journal, 56:4, 1319-1324 [1992]; F. Awal, L. Kluge, R. Kluge, J. Abadia in Iron Nutrition in Soils and Plants, Proceedings of the Seventh International Symposium, Zaragoza, Spain, June 27 to July 2, 1993, Kluwer Academic Publishers: Dordrecht, 1995, 53-62; J.J. Mortvedt, R.L. Mikkelsen, A.D. Behel Jr., Journal of Plant Nutrition, 15:10, 1913-1926 [1992]).

Surprisingly it was found that when cross-linked poly(meth)acrylates are added to substrates contaminated with heavy metals, the plant availability of heavy metals is distinctly reduced or even completely eliminated.

Heavy metals contained in the substrates are captured by the negatively charged carboxyl groups of the poly(meth)acrylates, which means that they are no longer available to the plants. This effect remains active over a long period of time, surprisingly as long as many months. In particular, this was unexpected by persons skilled in the art, and it allows a long-term elimination of the effect which heavy metals have in contaminated soils.

The substrates, such as soils or hydrocultures, are treated with the cross-linked poly(meth)acrylates, in particular by mixing in quantities of 0.1% to 2.5% in relation to the total substrate weight, preferably quantities of 0.5% to 2%, in particular about 0.2% to 0.8%, and specifically 0.4% to 0.6%.

The soil is excavated to a depth of up to about 50 cm, preferably 30 cm, and in particular about 40 cm, and mixed with the poly(meth)acrylates.

Suitable poly(meth)acrylates that can be used according to the invention are all cross-linked poly(meth)acrylates which contain carboxylate groups and form hydrogels.

Particularly to be used according to the invention are poly(meth)acrylates which contain carboxylate groups and consist preferably of the monomers acrylic acid, acrylamide, methacrylic acid and methacrylamide, but also other water-soluble monomers such as acrylonitril, methacrylonitril, N,N-dimethylacrylamide, vinyl pyridine and other water-soluble polymerizing acids and their salts, in particular maleic acid, fumaric acid, itaconic acid, vinylosulfonic acid or acrylamidomethylolpropanosulfanic acid; also the esters which contain hydroxy groups and belong to the polymerizing acids, in particular the hydroxyethyl esters and hydroxypolyesters of acrylic acid and of methacrylic acid; also the esters and amides which contain amino groups and ammonium groups and belong to the polymerizing acids such as dialkylamino ester, in particular the dimethyl esters and the diethylaminoalkylic esters of acrylic acid and of methacrylic acid, as well as the trimethyl esters and the trimethylammoniumalkyl esters and the corresponding amides. The poly(meth)acrylates to be used according to the invention can consist exclusively of the above named monomers containing carboxylate groups or can be combined in a copolymerisate with monomers containing no carboxylate groups. In the copolymers, the rate of carboxylate monomers is at 90 to 10 mol percent, preferably at 60 to 30 mol percent.

In addition, monomers of little or no water solubility can be copolymerized in small amounts with the above named monomers, such as vinyl esters and the esters of acrylic acid and/or methacrylic acid with C₁-C₁₀ alcohols, styrol and alkylated styrols. In general, the proportion of water-insoluble monomers is about 80 to 100 % by weight, related to the totality of monomers. As a rule, the water-insoluble (hydrophobic) monomers form 0 to 20% by weight of the monomers.

The acidic monomer components can be neutralized prior to polymerization, whereby the degree of neutralization is preferably between 10 and 95 mol percent, in particular between 50 and 90 mol percent, and especially between 70 and 95 mol percent. Bases used in neutralization can be any of the customary inorganic and organic compounds, preferably caustic soda solution, caustic potash solution and ammonia (ammonium hydroxide).

Together with the above named monomers, small amounts of cross-linking monomers are copolymerized with more than one

reactive group in the molecule. This results in partially cross-linked polymerizates which are no longer soluble but only swellable in water. Among the cross-linking monomers that can be used are, for example, the following bifunctional or multifunctional monomers: amides such as methylenebisacrylic or methylenemethacrylic amide, allylic compounds such as allyl(meth)acrylate, alkoxylated allyl(meth)acrylate preferably reacted with 1 to 30 mol ethylene oxide, triallylocyanurate, maleic-acid diallyl ester, polyallyl ester, tetraallyloxiethane, triallylamine, tetraallylethylenediamine, allyl ester of phosphoric or phosphorous acid, also cross-linking monomers such as N-methylol compounds of amides such as methacrylamide or acrylamide and the ethers derived therefrom, and esters of polyols and alkoxylated polyols such as diacrylates or triacrylates such as butanediol or ethylenoglukolodiacrylate, polyglylkol-di-(meth)acrylate, trimethylolopropiontriacrylate, diacrylate and triacrylate esters of trimethylolopropane - preferably oxalkylated (ethoxylated) with 1 to 30 mol of alkyleneoxide, acrylate ester and methacrylate ester of glycerin and pentaerythritol, as well as glycerin and/or pentaerythrite preferably oxethylated with 1 to 30 mol of ethyleneoxide. Preferred are methylen or ethylenbis(meth)acrylamides, N-methylolacrylamides and triallylamine. The proportion of cross-linking comonomers is about 0.01 to 2.5 % by weight, preferably about 0.01 to 1.0 % by weight, and especially preferred about 0.01 to 0.1% by weight, related to the totality of monomers.

The polymers according to the invention, which contain carboxylate groups, may contain water-soluble polymers as a graft base, whereby amounts up to 30% by weight are preferred. These include partly or fully saponified polyvinyl alcohols, starch or starch derivatives, cellulose or cellulose derivatives, lignin or lignin derivatives, polyacrylic acid, polyglycols or their mixtures.

In a preferred embodiment, the polymers to be used according to the invention are subsequently cross-linked. For subsequent cross-linking, which leads to a clear improvement in gel stability, liquid absorption under pressure, and absorption velocity, compounds are used which as a rule have at least two functional groups and which can cross-link the functional groups of the polymerizate on the surface of the polymer particles. Preferred are alcohol, amine, aldehyde, glycidyl and epichlor functions, whereby cross-linking molecules with various functions can be used. The following are named as examples: ethylenoglykol, diethylene glycol, triethylene glykol, polyethylene glykol, glycerin, polyglycerin, propylene glykol, diethanolamine, triethanolamine, polypropylene oxide, block copolymers of ethylene oxide and propylene oxide, sorbitan fatty acid ester, trimethylol propane, ethoxylated trimethylol propane, pentaerythritol, ethoxylated pentaerythritol, polyvinyl alcohol,

sorbite, ethylene carbonate, propylene carbonate and polyexpoxides such as ethylene glykol diglycidyl ether. Preferably, ethylene carbonate is used as a subsequent cross-linking agent. The subsequent cross-linking agent is used in amounts between 0,01 to 10% by weight, preferably 0,1 to 5% by weight, and especially 0,1 to 1% by weight related to the polymer to be subsequently cross-linked.

The poly(meth)acrylates to be used according to the invention can be produced by conventional means, but it is preferable to polymerize discontinuously in aqueous solution in a polymerization vessel or continuously, for example on a continuous belt. Polymerization is initiated with customary initiators or redox systems which initiate radical polymerization. In a practically adiabatic polymerization process, an aqueous polymer gel is formed with an appropriate initial monomer concentration of 15 to 50% by weight. By selecting the initial monomer concentration and an appropriately low starting temperature in the range of 0 to 50° C, preferably between 5 and 25° C, polymerization can be such that the maximum temperature in the aqueous polymer gel that forms can be well controlled. After completed polymerization, the polymer gel is mechanically reduced in size, dried, ground and if need be subjected to surface cross-linking.

Also suitable for producing poly(meth)acrylates is the suspension polymerization method, in which the discrete polymer particles are formed already during polymerization.

When the surface cross-linking agents are added, it must be ensured that the polymer particles are well mixed. Some suitable mixing devices for applying the subsequent cross-linking agent are the Patterson-Kelley Mixer, the DRAIS Turbulence Mixer, the Lödige Mixer, the Ruberg Mixer, screw mixers, disk mixers and fluid-bed mixers as well as continuously operating vertical mixers in which the powder is mixed at a rapid frequency by means of rotating knives (Schugi Mixer). After the subsequent cross-linking agent, preferably in the form of a solution, has been mixed with the polymer particles, the subsequent cross-linking reaction takes place at temperatures of 80 to 250° C, preferably at 135 to 250° C, and especially at 150 to 200° C. The optimal period of subsequent heating can be easily determined for the individual cross-linking agents by means of a few experiments. It is limited by the point at which the desired characteristic profile of the super-absorber is again destroyed due to heat damage. For example, the cross-linking periods for a temperature of 180° are usually below 30 minutes.

The poly(meth)acrylates may still contain processing and conditioning aids such as potassium stearate, polyglykol, silicic acids, bentonite, etc.

The residual content of the poly(meth)acrylates to be used according to the invention is low and amounts to less than 1000 ppm, preferably less than 500 ppm, and especially less than 250 ppm. In particular, the residual amount of monomers such as acrylamide, which are of ecological concern, is preferably below 250 ppm.

The absorption capacity of the poly(meth)acrylates to be used according to the invention for water and aqueous solutions may fluctuate within a wide range and is determined by the monomer components, the cross-linking agents and in some cases the subsequent cross-linking agents.

Preferably, the poly(meth)acrylates used are those which absorb more than 30 g/g, preferably more than 50 g/g and especially more than 65 g/g of polymer in a synthetic soil solution with a conductivity of 2.5 μ S. Per 10 litres of water, the synthetic soil solution contains 0.71 g NaCl, 0.065 g NaN₃, 1.676 g CCl, 0.353 g NH₄Cl, 3.363 g MgCl₂·6H₂O, 10.5 g CaCl₂·2H₂O and 0.010 g FeCl₃·6H₂O. In this solution, 1 g of poly(meth)acrylate is stirred with a magnetic stirrer for 15 minutes, allowed to stand for 45 minutes and then filtered over a 100 mesh sieve. The quotient of the absorbed amount of liquid and the weighed portion of polymer is the absorption value.

Copolymers of poly(meth)acrylates produced by using comonomers not containing carboxyl groups, especially acrylamide, have a higher long-term stability of absorption in terms of the frequently changing damp and dry phases during application.

The soluble components of the poly(meth)acrylates to be used according to the invention are usually below 20% by weight, preferably below 15% by weight, and especially below 10% by weight.

The particle-size distribution of the poly(meth)acrylates to be used may differ depending on the application, but normally it is in the 0.2 to 3 mm range.

Furthermore, the poly(meth)acrylates may be charged with active agents which they gradually release again into the environment in the course of application according to the invention. Among these agents are fertilizers, herbicides and pesticides.

The invention is described below in detail with reference to the following examples:

Example 1

Sterile-germinated Scotch pine (*Pinus sylvestris*) seedlings were grown in a sterile reconstituted soil solution (Table 1) from the Solling region, to which lead and cadmium chloride in

concentrations were added, each at a rate of 1 $\mu\text{mol/litre}$.

Table 1: Nutrient solution used, in $\mu\text{mol/litre}$
 Ca^{2+} : 130, K^+ : 350, Mg^{2+} : 82, Na^+ : 174, Fe^{3+} : 10;
 NO_3^- : 644, SO_4^{2-} : 85, PO_4^{3-} : 16, Cl' : 154 \AA

The experimental plants were sterile-germinated on agar plates where they were grown until the cotyledons developed. Subsequently they were transplanted into sterile hydrocultures which were kept under constant light conditions (photosynthetically active photon flow density of 170 $\mu\text{mol m}^{-2}\text{s}^{-1}$, at 16 hours of light/8 hours of darkness) and in a constant room climate (room temperature 22/20° C day/night). The nutrient solution was changed weekly.

After a growing period of 4 weeks in the nutrient solution without additives, the plants were treated with Stockosorb and heavy metals according to the design described below. During the treatment period, the nutrient solution was changed weekly.

In each experimental variant, 30 plants were used in three pots with 10 plants each. The individual pots were evaluated separately, and mean values were calculated for the individual pots as well as for the entire experimental variant. For the evaluation, the plants were photographed at the end of the experiment, the length of roots and shoots was measured, photosynthesis rates and dry weights of roots, shoots and needles were determined. The root was pulped, and the heavy-metal contents were determined in the atom absorption spectrometer (AAS).

Treatment design

K-Control, without heavy metals, without Stockosorb
K-Cd, Pb-Control with heavy metals, without Stockosorb
K-stock. 0.4%-Control with Stockosorb, without heavy metals
St. 0.04%-with 0.04% Stockosorb and heavy metals
St. 0.1%-with 0.1% Stockosorb and heavy metals
St. 0.4%-with 0.4% Stockosorb and heavy metals

- Fig. 1 shows the transpiration rates,
Fig. 2 shows assimilation,
Fig. 3 shows the absorption of lead,
Fig. 4 shows the absorption of cadmium

determined in the various experimental variants.

It is clear that treatment with Stockosorb has eliminated the toxic effect of the heavy metals and that their absorption by the plants has been retarded. Similar results were obtained in similar experiments with Aleppo pine and with a poplar species (*Populus hupehensis*).

Example 2

Three-year old spruce in 12-litre containers were planted into a loamy shale soil from the Hartz Mountains region, which had been treated with 0.6% Stockosorb K 400. Control experiments were planted simultaneously with untreated soil. The plants were kept outdoors from May to October; they were routinely watered with tap water.

Subsequently, the plants were exposed to a water-stress treatment, i.e. watering was stopped until the needles became gray and dropped.

From each treatment variant the fine roots of three different plants were removed and prepared for ion localization under the electron microscope (D.L. Godbold, E. Fritz, A. Hüttermann: Aluminum toxicity and forest decline. Proc. Natl. Acad. Sci. USA 85, 3888-3892 [1988]). Fig. 5 shows the analyses of lead contents in the cell walls of the root epidermis and the central cylinders (steles) of various roots. In the roots grown in the untreated soils, large amounts of lead were found in the cell walls of the cortex as well as in the stele (Fig. 5, Control). In the cell walls of the root epidermis of plants grown in the soils treated with Stockosorb, the lead content was lower (Fig. 5, +0.6% Stockosorb). Furthermore, considerably less lead was transported into the steles via the epidermis.

Stockosorb was effective even under very difficult conditions for the plants, when the soil was dried out and the ion concentration in the soil solution increased by at least one order of

magnitude.

Example 3

The roots of the plants in Example 2 were washed. As Fig. 6 shows, considerably more roots were formed in the soil treated with Stockosorb than by the plants growing in the control soils, whereby each of the five plants examined in the soils treated with Stockosorb, had formed four times more root mass than those grown in the control soils.

Claims

1. Process for reducing plant availability of heavy metals in substrates, characterized in that the substrates are treated with cross-linked polyacrylates or polymethacrylates.
2. Process according to Claim 1, characterized in that the substrates are treated by means of mixing.
3. Process according to Claim 2, characterized in that in mixing, the amount of additive is 0.1 to 2.5% by weight.
4. Process according to Claim 3, characterized in that in mixing, the amount of additive is 0.5 to 2.0% by weight.
5. Process according to Claim 1, characterized in that the cross-linked poly(meth)acrylates are produced by using monoethylenically unsaturated monocarboxylic acids, in particular acrylic acid or its salts.
6. Process according to Claim 5, characterized in that the poly(meth)acrylates are produced by using other monoethylenically unsaturated monomers containing no carboxylate groups, in particular by using acrylamide.
7. Process according to Claims 5 or 6, characterized in that the poly(meth)acrylates are obtained by using methylenbis(meth)acrylamide, ethylenbis(meth)acrylamide, N-methylolacrylamide or triallylamin as cross-linking agents, whereby methylenbisacrylamide is preferred.
8. Process according to one or more of Claims 5 to 7, characterized in that the poly(meth)acrylates are treated with a subsequent cross-linking agent in quantities of 0.01 to 10% by weight, at an increased temperature, preferably between 80 and 250° C.
9. Process according to one or more of Claims 5 to 8, characterized in that the acidic monomer components of the poly(meth)acrylate are neutralized between 10 and 95 mol percent, preferably between 50 and 90 mol percent.
10. Process according to one or more of Claims 5 to 9, characterized in that the poly(meth)acrylates have an absorption capacity for synthetic soil solution of more than 30 g/g, preferably more than 50 g/g, and especially more than 65 g/g.
11. Process according to one or more of Claims 5 to 10, characterized in that the poly(meth)acrylates are worked into the acid soil up to a depth of about 50 cm.
12. Use of cross-linked poly(meth)acrylates to reduce plant

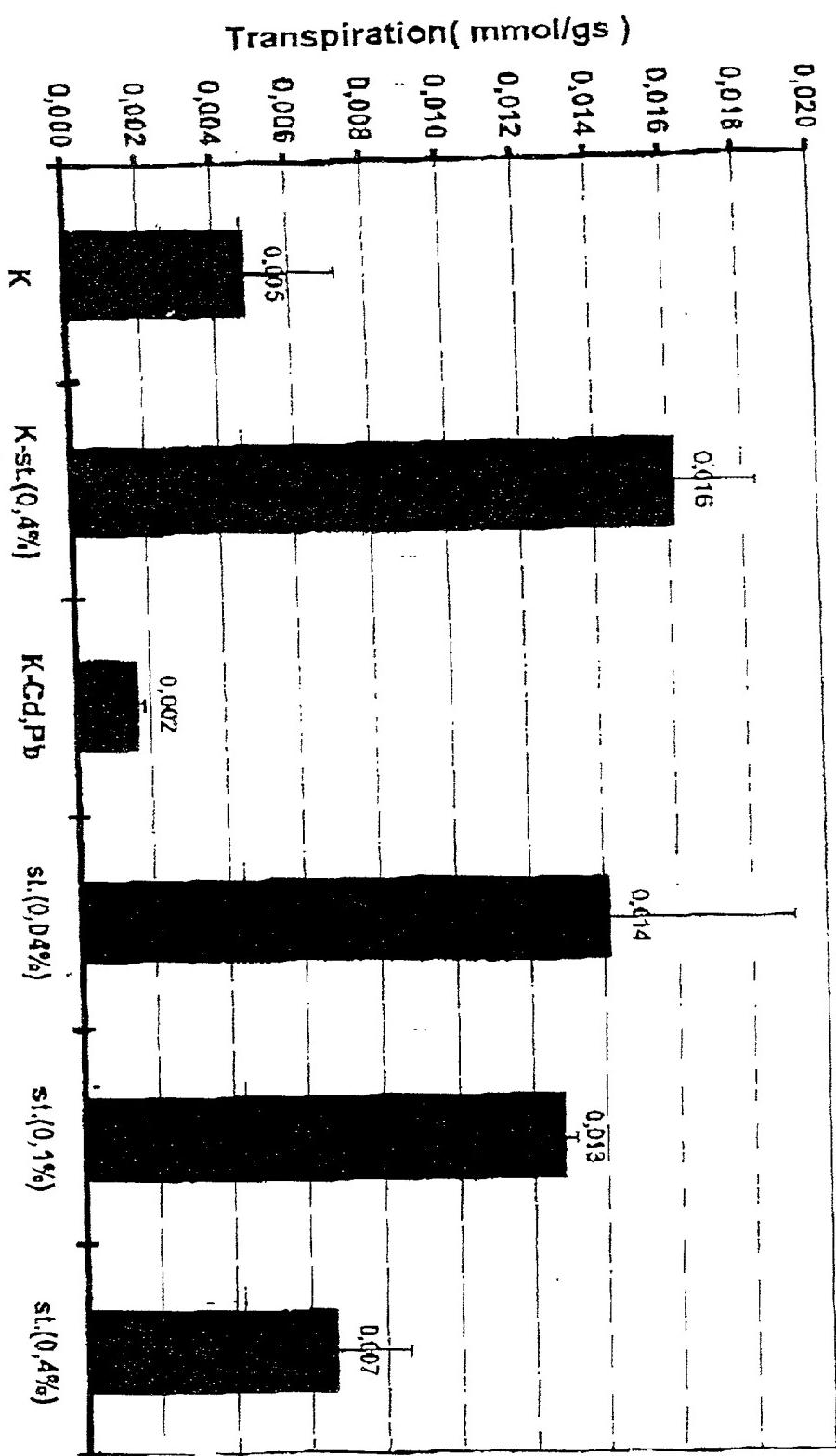
availability of heavy metals in substrates such as soils or culture solutions.

Abstract

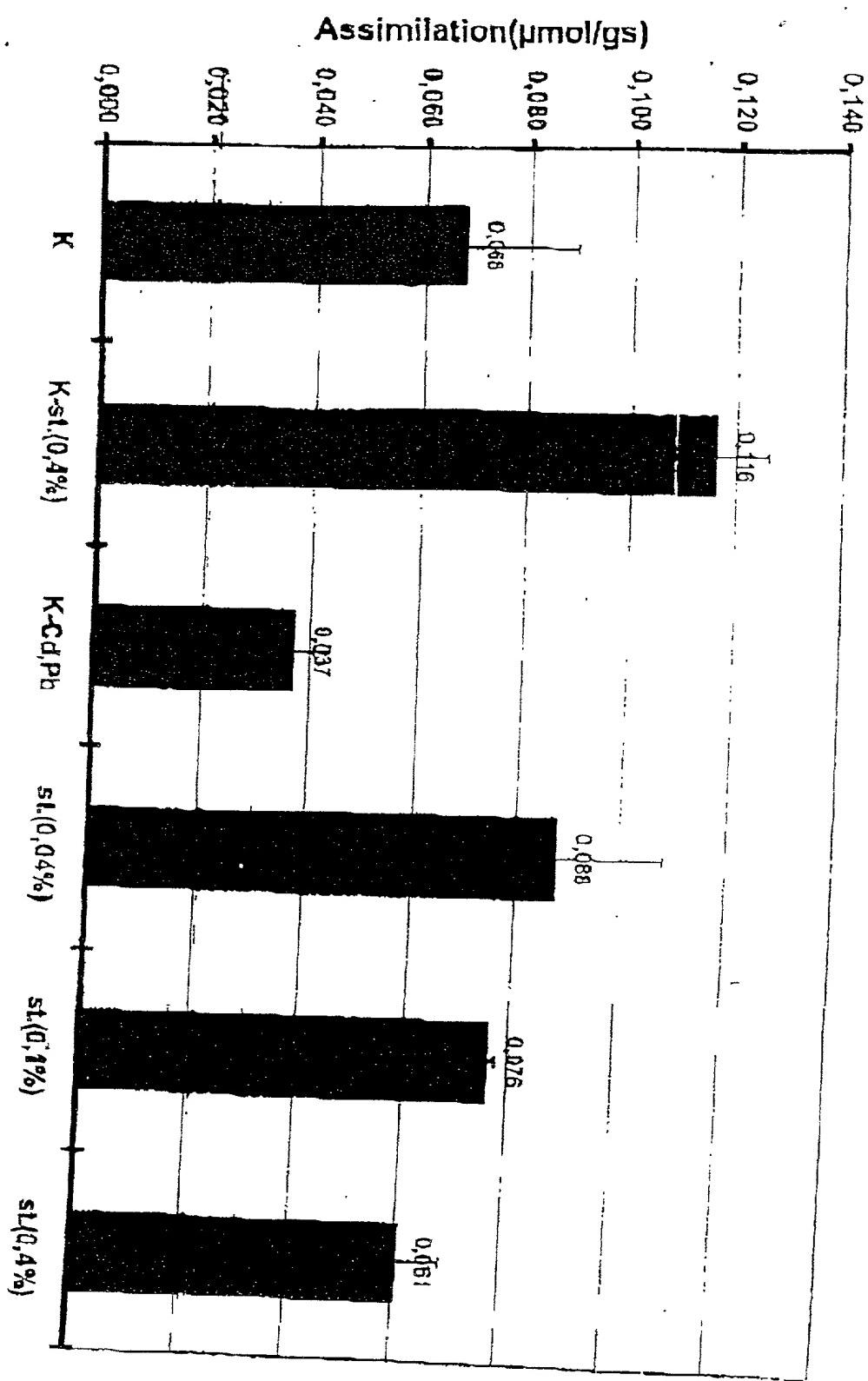
A process for reducing plant availability of heavy metals in substrates such as soils is characterized in that the substrates are treated with cross-linked polymethacrylates. The poly(meth)acrylates can be worked into the soils.

- Fig. 1 Transpiration (*Pinus sylvestris*)
Behandlungen = treatments
- Fig. 2 Assimilation (*Pinus sylvestris*)
Behandlungen = treatments
- Fig. 3 Lead absorption (*Pinus sylvestris*)
Pb-Gehalt (mg/kg Wurzel TG) = Pb content (mg/kg of root dry weight)
Behandlungen = treatments
- Fig. 4 Cadmium absorption (*Pinus sylvestris*)
Cd-Gehalt (mg/kg Wurzel TG) = Cd content (mg/kg of root dry weight)
Behandlungen = treatments
- Fig. 5 Kontrolle = Control
Bleigehalt . . . = Lead content in the cell wall (mmol/dm³)
- Fig. 6 Root stock of spruce grown in lead-contaminated soil treated with Stockosorb (left) in comparison with untreated control (right)

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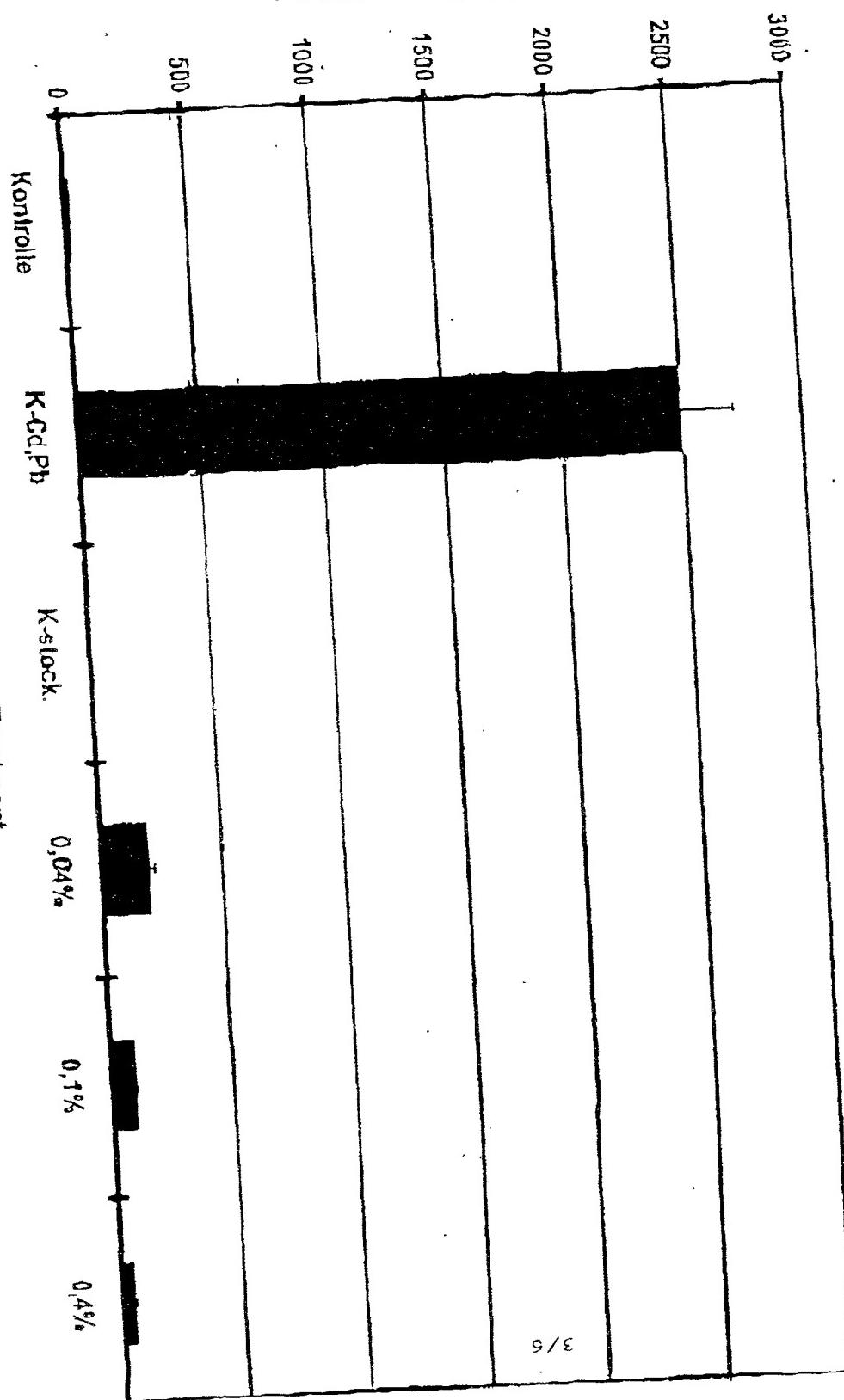
FIG. 1 Transpiration (*Pinus sylvestris*)

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Fig. 2 Assimilation (*Pinus sylvestris*)

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PB-Content (mg/kg (tree) root/TG)

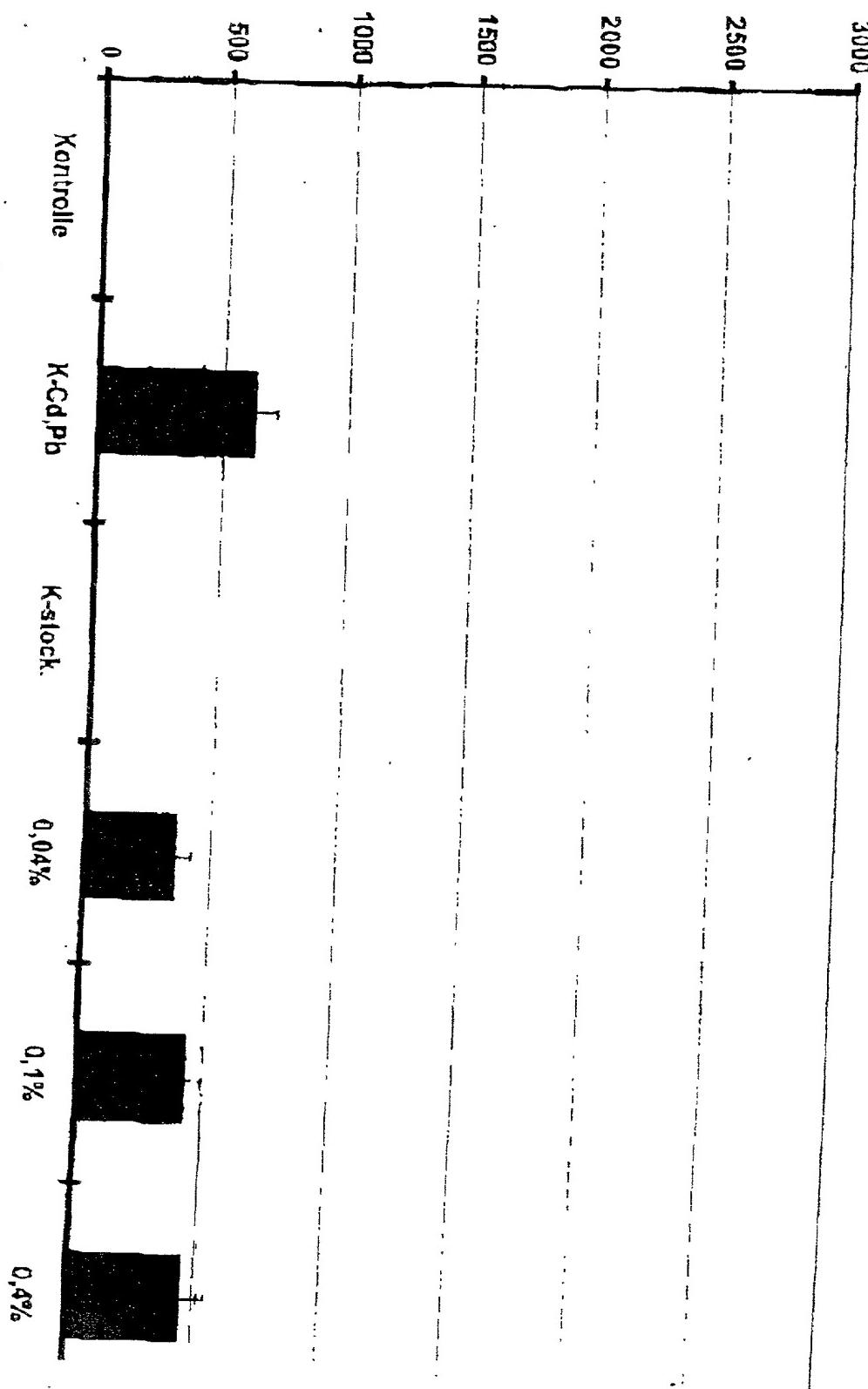
Fig. 3 Lead-Uptake (*Pinus sylvestris*)

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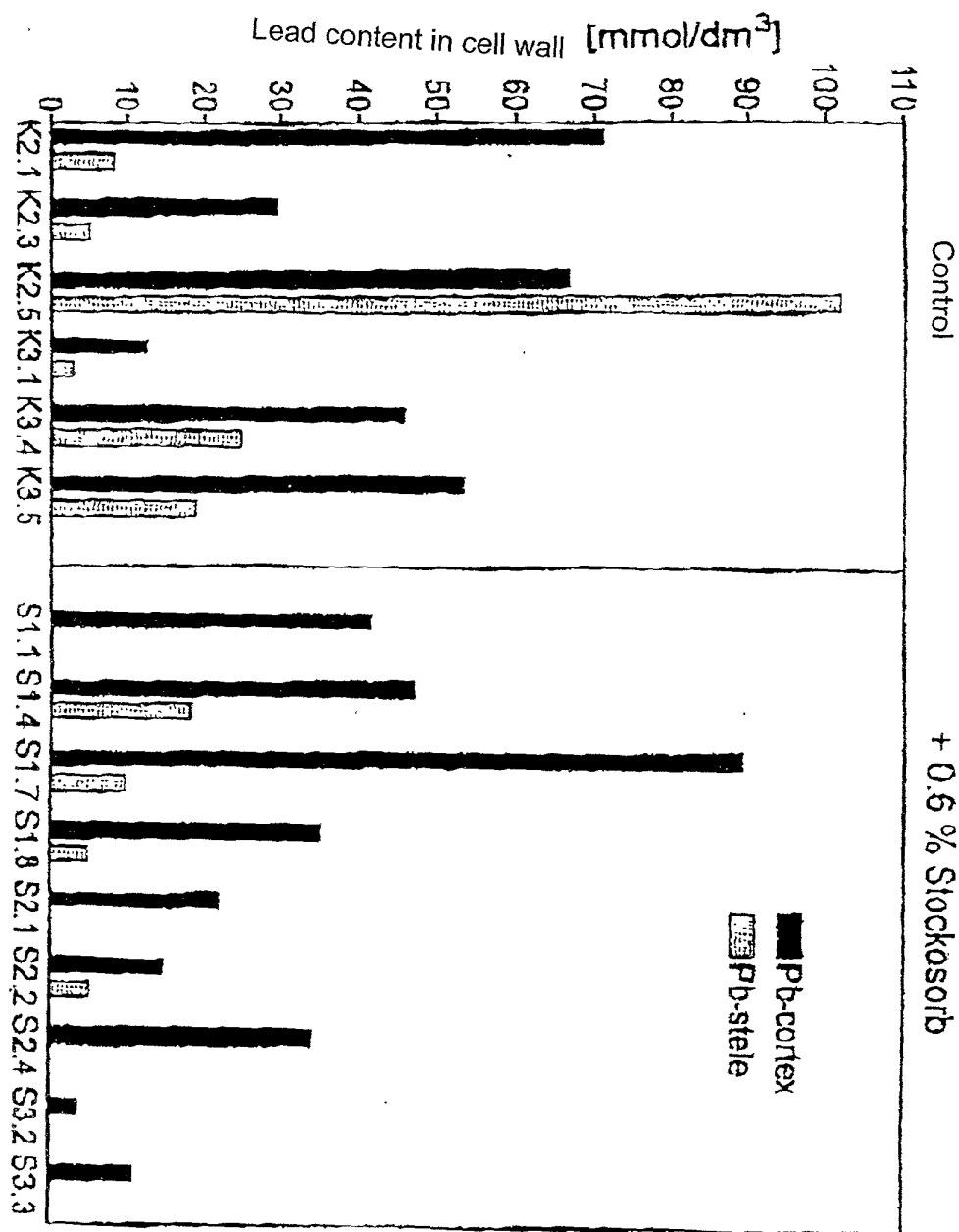
Cd- Content (mg/kg (tree) root/TG)

Fig. 4

Cadmium-Uptake (*Pinus sylvestris*)



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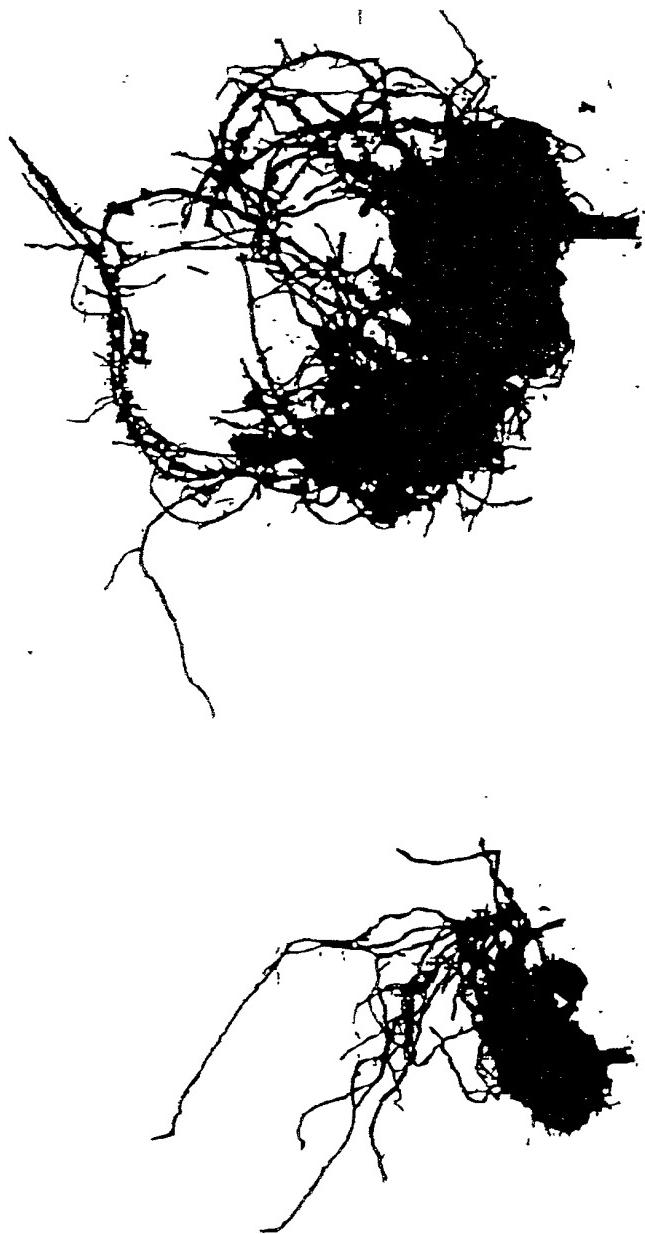


Fig. 6:

Root system of spruce which are grown in lead-containing soil treated with Stockabsorb (left) in comparison to untreated control (right)

COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY
Includes Reference to PCT International Applications

Attorney's Docket
No.3395-4PUS

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

**METHOD OF REDUCING THE AVAILABILITY OF HEAVY METALS IN PLANTS AND THE USE OF CROSS
LINKED POLY(METH)ACRYLATES IN SAID METHOD**

the specification of which (check only one item below)

is attached hereto

was filed as United States application

Serial No.

on

and was amended

on (if applicable).

as filed as PCT international application

Number PCT/EP99/02008 ✓

on 24 March 1999

and was amended under PCT Article 19

on (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the patentability of the application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed.

PRIOR FOREIGN/PCT APPLICATIONS AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. 119:

Country (if PCT, indicate "PCT")	Application Number	Date of Filing (day, month, year)	Priority Claimed Under 35 U.S.C. 119	
Germany ✓	198 13 425.8 ✓	26 March 1998 ✓	<input checked="" type="checkbox"/> YES	<input type="checkbox"/> NO
PCT	PCT/EP99/02008	24 March 1999	<input checked="" type="checkbox"/> YES	<input type="checkbox"/> NO
			<input type="checkbox"/> YES	<input type="checkbox"/> NO
			<input type="checkbox"/> YES	<input type="checkbox"/> NO
			<input type="checkbox"/> YES	<input type="checkbox"/> NO
			<input type="checkbox"/> YES	<input type="checkbox"/> NO

Combined Declaration for Patent Application and Power of Attorney (Continued)
 (Includes Reference to PCT International Applications)

Attorney's Docket
 3395-4PUS

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that/those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application(s) and the national or PCT international filing date of this application:

PRIOR U.S. APPLICATIONS OR PCT INTERNATIONAL APPLICATIONS DESIGNATING THE U.S. FOR BENEFIT UNDER 35 U.S.C. 120:

U.S. APPLICATIONS		STATUS (check one)		
U.S. APPLICATION NUMBER	U.S. FILING DATE	PATENTED	PENDING	ABANDONED
PCT APPLICATIONS DESIGNATING THE U.S.				
PCT APPLICATION NO.	PCT FILING DATE	U.S. SERIAL NUMBERS ASSIGNED (if any)		
PCT/EP99/02008	24 March 1999			

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith (*List name and registration number*)

MYRON COHEN, Reg. No. 17,358; THOMAS C. PONTANI, Reg. No. 29,763; LANCE J. LIEBERMAN, Reg. No. 28,437; MARTIN B. PAVANE, Reg. No. 28,337; MICHAEL C. STUART, Reg. No. 35,698; KLAUS P. STOFFEL, Reg. No. 31,668; EDWARD M. WEISZ, Reg. No. 37,257; JULIA S. KIM, Reg. No. 36,567; VINCENT M. FAZZARI, Reg. No. 26,879; ALFRED W. FROEBRICH, Reg. No. 38,887; KENT H. CHENG, Reg. No. 33,849; GEORGE WANG, Reg. No. 41,419; TZVI HIRSHAUT, Reg. No. 38,732; GERALD J. CECHONY, Reg. No. 31,335; ROGER S. THOMPSON, Reg. No. 29,594; JOY I. FARBER, Reg. No. 44,103; and George J. Brandt, Jr., Reg. No. 22,021.

Send correspondence to:

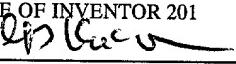
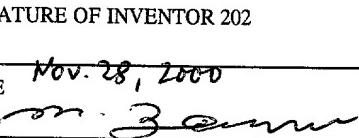
Thomas C. Pontani
Reg. No. 29,763
Cohen, Pontani, Lieberman & Pavane
551 Fifth Avenue, Suite 1210
New York, New York 10176

Direct Telephone calls to:
 (name and telephone number)
Thomas C. Pontani
(212) 687-2770

1-002	FULL NAME OF INVENTOR	FAMILY NAME <u>HÜTTERMANN</u>	FIRST GIVEN NAME <u>Aloys</u>	SECOND GIVEN NAME
01	RESIDENCE, CITIZENSHIP	CITY <u>Göttingen</u>	STATE OR FOREIGN COUNTRY <u>Germany</u>	COUNTRY OF CITIZENSHIP <u>Germany</u>
1	POST OFFICE ADDRESS	POST OFFICE ADDRESS <u>Henry-Dunant-Str. 20</u>	CITY <u>Göttingen</u>	STATE & ZIP CODE/COUNTRY <u>Germany 37075</u>
2-002	FULL NAME OF INVENTOR	FAMILY NAME <u>ZOMORRODI</u>	FIRST GIVEN NAME <u>Moitoba</u>	SECOND GIVEN NAME
2	RESIDENCE, CITIZENSHIP	CITY <u>Göttingen</u>	STATE OR FOREIGN COUNTRY <u>Germany</u>	COUNTRY OF CITIZENSHIP <u>Germany</u>
2	POST OFFICE ADDRESS	POST OFFICE ADDRESS <u>Auf der Lieth 14</u>	CITY <u>Göttingen</u>	STATE & ZIP CODE/COUNTRY <u>Germany 37077</u>

Combined Declaration for Patent Application and Power of Attorney (Continued) (Includes Reference to PCT International Applications)				Attorney's Docket 3395-4PUS
2 0 3	FULL NAME OF INVENTOR	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME
	RESIDENCE, CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP
	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under §1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

SIGNATURE OF INVENTOR 201 	SIGNATURE OF INVENTOR 202 	SIGNATURE OF INVENTOR 203
DATE Nov. 28, 2000	DATE Nov. 28, 2000	DATE 